Belcher

MATERIALS RESEARCH SOCIETY MEETING:

Assembling the Supersmall and Ultrasensitive

Robert F. Service

BOSTON, MASSACHUSETTS--Graced by unseasonably mild temperatures, about 3500 materials scientists, chemists, and physicists gathered here for the semiannual Materials Research Society (MRS) meeting.* Hot topics included reports of using viruses to assemble nanoparticles and of novel composites that pave the way for ultrasensitive sensors.

Liquid Crystals Via Virus

Angela Belcher doesn't just borrow ideas from biology in making new materials--she borrows whole organisms. At the MRS meeting, Belcher, a chemist at the University of Texas, Austin, described making liquid crystalline films out of viruses engineered to tote tiny inorganic nanoparticles. Polymer-based liquid crystalline films already form the heart of flat-screen computer displays. And although the viral liquid crystals aren't likely to displace their polymer counterparts anytime soon, they point the way forward in one of the hottest areas of materials science, merging the organizational prowess of biology with the electronic, magnetic, and structural properties of inorganic compounds.

Liquid crystals, first discovered in 1888, have molecular structures that are poised between the rigid order of solid crystals and the bumper-car chaos of liquids. Displaymakers use this malleability to their advantage: By applying an electric field, they reorient the liquid crystal, a change that switches the material from transparent to opaque. In Belcher's experiments, the viruses take on the ordering duties themselves. "The virus is making the liquid crystal and orienting it," says materials scientist Samuel Stupp of Northwestern University in Evanston, Illinois.

Self-assembly. An atomic-force microscope image (*right*) shows that pencil-shaped viruses toting nanoparticles have stacked themselves like cordwood.

CREDIT: ANGELA BELCHER/UNIVERSITY OF TEXAS

Viral films aren't Belcher's first foray into using living organisms to make materials. Two years ago, Belcher and her Texas colleagues reported that viruses could be engineered to express, for example, proteins that bind semiconductor nanoparticles made from gallium arsenide but not silicon or cadmium selenide (*Science*, 24 December 1999, p. 2442). That work held out hope that microbes could eventually help researchers shepherd nanoparticles into complex arrangements that are possibly useful for storing electronic data or wiring up molecule-sized electronic devices. The new work brings such potential applications much closer, as it shows for the first time that biological systems can organize nanoparticles into macrosized structures.

To make the films, Belcher and her graduate student Seung-Wuk Lee started by inserting random mutations into the viral DNA for a protein that sits on one outer tip of long, pencil-shaped viruses. When the viruses infected their bacterial hosts, they reproduced and expressed the engineered protein on their coat. The researchers then turned the viruses loose in a solution containing nanoparticles made of zinc selenide. The best nanoparticle-binding virus was then allowed to reproduce, making billions of copies. Finally, by simply changing the concentration of the viruses in solution, Belcher and Lee found that they could coax the viruses to pack themselves and their nanoparticle cargoes together in different liquid crystalline arrangements. The viruses' ability to form films "was a surprise to us," says Belcher.

In one such film, for example, the viruses lined up in successive rows, like rows of pencils all with zinc selenide erasers at one end (see figure above). Other films have viruses lining up in either a zigzag pattern or all facing the same direction but not organized into orderly rows. And each arrangement, Belcher's team found, produced unique iridescent patterns when viewed with a microscope under polarized light, a common characteristic of liquid crystalline films. Unlike polymer liquid crystals, however, the viral films cannot yet be easily switched between different configurations.

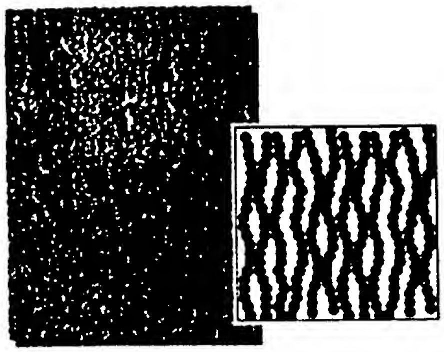
Although the new films' optical properties make them visually striking, their ability to align nanoparticles over relatively large distances could be even more important in the long run. Stupp points out that nanoscience researchers have developed numerous techniques to pattern nanoparticles and other nanosized objects at small-length scales. Extending such patterns to the macroscale has proven difficult. But because the Texas team's viruses can assemble themselves into films that can be picked up with a pair of tweezers, they may offer researchers new ways to stack metallic nanoparticles into nanowires or magnetic nanoparticles for data storage.

Swell New Sensor

Whether we notice them or not, sensors that detect small changes in temperature, pressure, and even the presence of chemicals are all around us. Many of them spot changes in their environment by tracking the effect on a material's ability to conduct electricity. Increase the temperature or pressure of the material, for example, and the conductivity can drop by about 50% to 90%. At the meeting, Jim Martin, a physical chemist at Sandia National Laboratories in Albuquerque, New Mexico, unveiled a plastic material embedded with magnetic particles that does quite a bit better, changing its conductivity as much as 100- billion-fold. And it's versatile, responding not only to temperature and

pressure changes but to the presence of some chemicals as well.

That sensitivity is "off the charts," says Todd Christenson, an electrical engineer and sensors expert at Sandia who is not affiliated with Martin's group. "It's incredible." That could ultimately make the new materials useful in a wide range of ultrasensitive detectors.



Power lines. Conducting particles aligned by a magnetic field offer sharp warnings of changes that break their connections.

CREDITS: J. MARTIN/SANDIA NATIONAL LABORATORIES

Martin got interested in the sensing ability of plastic composites after hearing a talk about the way some commercial sensors work. Those sensors harbor a random mixture of tiny conductive carbon particles in an insulating polymer matrix sandwiched between two electrodes. Flip the switch, and current hops between connecting carbon particles. But jack up levels of a property such as temperature and the polymer swells, breaking the contact between some of the carbon particles and causing the conductivity to drop. Such devices can vary widely and unpredictably in performance, however, because each winds up with a different ordering of carbon particles, Martin says.

Martin suspected that researchers could make the sensors more sensitive and reliable by stringing the conducting particles between the electrodes like tiny wires. In that arrangement even slight environmental changes would change the polymer enough to knock the particle chains out of alignment. To get that alignment, Martin's team decided to use a magnetic field, which causes magnetic particles to line up in the direction of the field lines (see figure at above). Because carbon particles aren't magnetic, the Sandia researchers used nickel particles, each about 2 millionths of a meter across. They electroplated each particle with a thin layer of gold to prevent the nickel from oxidizing when exposed to air, a change that would destroy the particle's conductivity. They then embedded their gold-coated nickel particles in an uncured polymer and exposed the combo to an external magnetic field. Once the particles were aligned in chains, the researchers cured the polymer and began their tests.

The results were dramatic. Bumping up the temperature just 5 degrees Celsius slashed the electrical resistance by five orders of magnitude. An 80-degree change made it plummet by 10 orders of magnitude. Modest pressure changes produced an effect of 11 orders of magnitude. And even exposing the polymer to a chemical vapor of toluene caused the polymer to expand and altered the resistance by nine orders of magnitude. "We were surprised by how well it worked," Martin says.

Martin says he has no immediate plans to commercialize the materials: "We're still at the level of science." Some bugs still remain to be ironed out as well. For example, many of the particles oxidize over time when exposed to air, probably a result of incomplete electroplating. But once the composites are fine-tuned, they are likely to be a hot commercial property, Christenson predicts.

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* 26-30 November.

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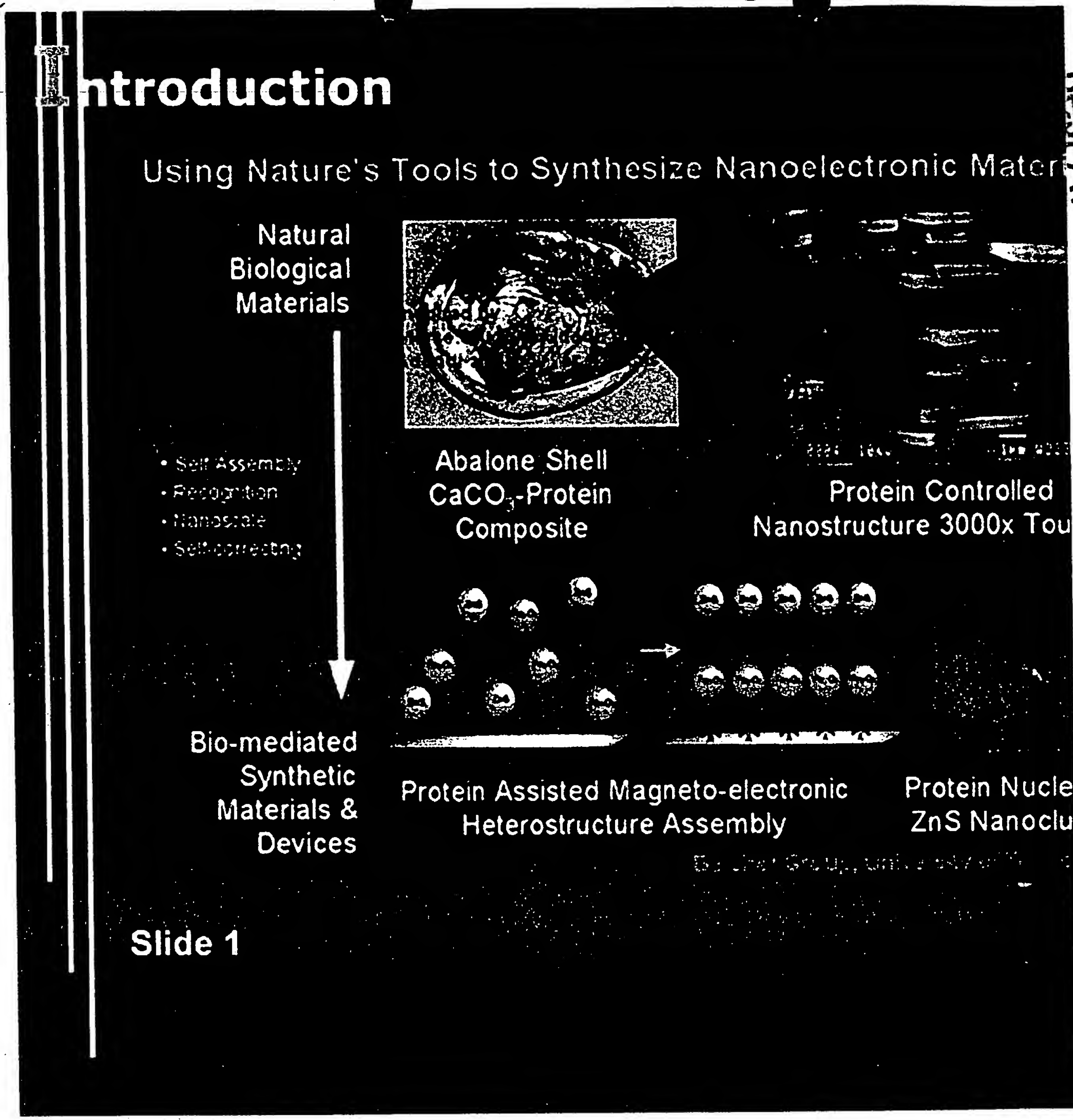
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NANOSCIENCE

VIRUS ASSEMBLES NANOPARTICLES

New way to order inorganic materials on macroscale borrows from nature

AMANDA YARNELL

Harnessing the organizational power of biology, chemists at the University of Texas, Austin, have developed a facile new way to precisely order nanoparticles on the macroscale. Assistant professor Angela M. Belcher, graduate student Seung-Wuk Lee, and coworkers find that viruses engineered to bind zinc sulfide quantum dots self-assemble into highly ordered, three-dimensional liquid-crystal films [*Science*, **296**, 892 (2002)].

The researchers genetically engineered a bacteriophage to create a library of peptides expressed on one tip of the rod-shaped virus. They then screened this library for viruses with affinity for a ZnS surface. The virus carrying the best ZnS-binding peptide was selected and mass-produced in its bacterial host.

ZIGZAG An atomic-force microscope image of the surface of the liquid-crystal film shows ZnS-tipped rodlike viruses lined up in a herringbone pattern, creating precisely spaced rows of ZnS quantum dots.
COURTESY OF SEUNG-WUK LEE

When this virus was mixed with a solution of ZnS precursors,

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the resulting ZnS-tipped viruses self-assembled into liquid-crystal films. By changing the solution concentration, the researchers made films with different virus arrangements--for example, rod-shaped viruses lined up end to end or organized in a herringbone pattern--each with a unique ordering of ZnS quantum dots.

Viruses could be similarly engineered to organize other electronic, optical, and magnetic materials, Belcher says. She and her coworkers are now screening for viruses that bind CdS, CdSe, ZnSe, Co, CoPt, and FePt.

A number of techniques have been used to create similar patterns of nanostructures. In an accompanying commentary, chemistry professor Christopher K. Ober of Cornell University notes that the viral assembly method--which yields centimeter-long liquid-crystal films--may make it easier to extend such features over relatively large dimensions.

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